

1 **POLYMERIC DISPERSANTS PREPARED**
2 **FROM COPOLYMERS OF LOW MOLECULAR WEIGHT**
3 **POLYISOBUTENE AND UNSATURATED ACIDIC REAGENT**

4
5 **BACKGROUND OF THE INVENTION**

6 This invention is directed to a new low molecular weight copolymer
7 (The PIB/UAR copolymer) that may be prepared by reacting a low molecular
8 weight polyisobutene (PIB) having less than about 32 carbon atoms with an
9 unsaturated acidic reagent in the presence of a free radical initiator. No chain
10 transfer agent is required to prepare the low molecular weight PIB/UAR
11 copolymer. The PIB/UAR copolymer may be useful as is, or as an
12 intermediate for (1) polysuccinimides, (2) detergents or dispersants for lube oil
13 or fuels, (3) pour point depressants and (4) surface sizing agents for paper.
14 The PIB/UAR copolymer may be used by itself or as the ester, amide, imide
15 or metal salt derivative of the PIB/UAR copolymer. Preferred PIB/UAR
16 copolymers are liquid at ambient temperature.

17 It is known that olefin/unsaturated acidic reagent copolymer
18 compositions may be prepared by reacting an alpha olefin with an
19 unsaturated acidic reagent in the presence of a free radical initiator. This
20 reaction is typically carried out at elevated temperatures either neat or in a
21 solvent or diluent. When the reaction is carried out neat, the resultant
22 copolymers have a high degree of polymerization, which results in a
23 high carbon number and a high molecular weight.

24 Traditionally, if a lower degree of polymerization, lower carbon number
25 or low molecular weight for a copolymer was desired; it was necessary to use
26 a chain transfer agent during the copolymer preparation to promote chain
27 transfer. This is because the chain transfer agent causes such copolymers to
28 have a lower degree of polymerization, which results in a lower carbon
29 number and a lower molecular weight.

30 A high temperature of reaction may be used alone or in combination
31 with chain transfer agents to encourage a low degree of polymerization and
32 the resulting low carbon number and low molecular weight. Traditionally, the
33 key factors used to influence the degree of polymerization for a

1 copolymerization reaction were combining high temperature and particular
2 chain transfer agents selected for the degree of polymerization they impart.

3 One draw back to using an alpha olefin to prepare the copolymer is
4 that the resulting copolymer is typically a glassy solid. A solid copolymer is
5 undesirable because a solid copolymer cannot be handled easily or pumped
6 readily at ambient temperatures. Before further processing, a solid copolymer
7 has to be brought to a consistency that may be pumped readily. This may be
8 accomplished by heating the solid copolymer to a temperature above the
9 melting point or using a solvent to dissolve it. Heating the copolymer is often
10 costly, and the addition of a solvent is often not practical. This is because it is
11 desirable to remove the solvent before the copolymer can be used, and the
12 solvent has to be disposed of in a manner consistent with environmental
13 regulations.

14 The PIB/UAR copolymer is an improvement over alpha olefin
15 copolymers in two respects. Surprisingly, a chain transfer agent is not
16 required to prepare the PIB/UAR copolymer at the desired low molecular
17 weight. Further, since the PIB/UAR copolymer is liquid, it is not necessary to
18 dissolve the PIB/UAR copolymer by using additional heat or adding solvent
19 before the PIB/UAR copolymer is used. Since no solvent is required, the step
20 of removing the solvent is not necessary either.

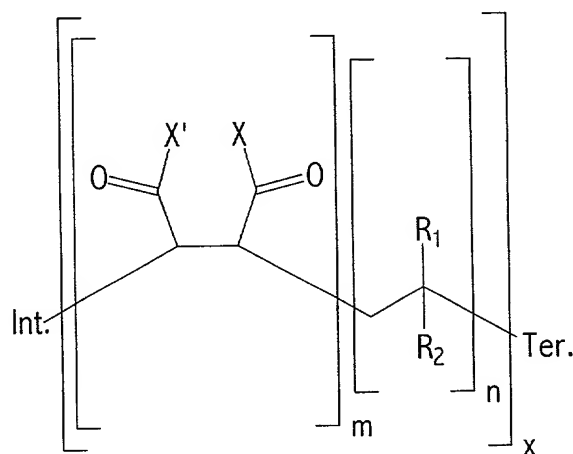
21 Preparing a polysuccinimide by reacting a PIB/UAR copolymer with a
22 polyamine and an alkenyl or alkyl succinic acid derivative offers several
23 advantages over preparing a polysuccinimide by reacting alpha olefin
24 prepared copolymers with polyamines and alkenyl or alkyl succinic acid
25 derivative. These advantages include: (1) no chain transfer agent is required
26 to produce the PIB/UAR copolymer having the desired low molecular weight,
27 and (2) since the PIB/UAR copolymer is liquid, it does not require melting or
28 the addition of a solvent before it can be used to make a polysuccinimide and
29 (3) since solvent is not required, the solvent does not have to be removed
30 thus eliminating handling or disposal cost.

31 32 SUMMARY OF THE INVENTION

33 This invention is directed to a new low molecular weight copolymer
34 (The PIB/UAR copolymer) that may be prepared by reacting a low molecular

weight polyisobutene (PIB) having less than about 32 carbon atoms with an unsaturated acidic reagent in the presence of a free radical initiator. No chain transfer agent is required to prepare the low molecular weight PIB/UAR copolymer. The PIB/UAR copolymer may be useful as is, or as an intermediate for (1) polysuccinimides, (2) detergents or dispersants for lube oil or fuels, (3) pour point depressants and (4) surface sizing agents for paper. The PIB/UAR copolymer may be used by itself or as the ester, amide, imide, or metal salt derivative of the PIB/UAR copolymer. The PIB/UAR copolymer may be liquid at ambient temperature.

This invention comprises one or more PIB/UAR copolymers having the general formula:

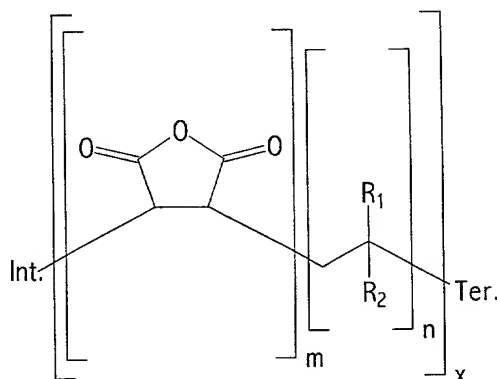


wherein
X and X' comprise one or more of: —OH; —O—hydrocarbyl; —NH₂; —Cl; —Br; —OM⁺, wherein M⁺ comprises one equivalent of at least one of a metal, ammonium and amine cation; and X and X' taken together as —O—;
n comprises a whole integer from 1 to 3; R₁ comprises methyl; R₂ comprises polyisobutyl having less than 32 carbon atoms; m comprises a whole integer of from 1 to 3; x comprises a whole integer of from 1 to 20; Int. comprises at least one initiating radical; and Ter. comprises at least one terminating group. The PIB/UAR copolymer may include either R₁ and R₂ that comprises

1 methyl and the other of R1 and R2 that comprises polyisobutyl having about 5
2 to about 25 carbon atoms. The PIB/UAR copolymer may be liquid at ambient
3 temperature. The PIB/UAR copolymer may comprise one or more of an
4 amide derivative, an ester derivative, an imide derivative and a metal salt
5 derivative. The PIB/UAR copolymer may have an average degree of
6 polymerization of about 1.1 to about 20. The PIB/UAR copolymer may have a
7 number average molecular weight of about 231 to about 10,920.

8 The PIB/UAR copolymer may be prepared by the polymerization of one
9 or more unsaturated acidic reagents and one or more polyisobutenes having
10 less than about 32 carbon atoms in the presence of one or more free radical
11 initiators. This unsaturated acidic reagent may comprise maleic anhydride.
12 The polyisobutene may comprises a mixture further comprising about
13 5 wt. % to about 20 wt. % C_8H_{16} ; about 35 wt. % to about 55 wt. % $C_{12}H_{24}$;
14 about 20 wt. % to about 30 wt. % $C_{16}H_{32}$; about 8 wt. % to about 15 wt. %
15 $C_{20}H_{40}$; about 2 wt % to about 8 wt % $C_{24}H_{48}$; and about 0.5 wt % to about
16 2 wt. % $C_{28}H_{56}$. The polyisobutene may also comprise a mixture having a
17 number average molecular weight (M_n) of about 150 to about 240. The
18 PIB/UAR copolymer may be prepared by performing a first step of reacting a
19 first amount of unsaturated acidic reagent with a first amount of polyisobutene
20 having less than about 32 carbon atoms, more preferably less than about
21 28 carbon atoms, in the presence of a first amount of free radical initiator to
22 form a first liquid PIB/UAR copolymer and a second step of reacting a portion
23 of the first liquid PIB/UAR copolymer with a second amount of unsaturated
24 acidic reagent, a second amount of polyisobutene having less than about 32
25 carbon atoms, more preferably less than about 28 carbon atoms, in the
26 presence of a second amount of free radical initiator.

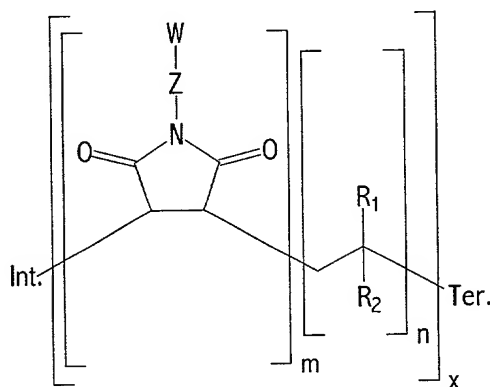
1 The PIB/UAR copolymer of this invention may also comprise one or
2 more copolymers having the general formula:



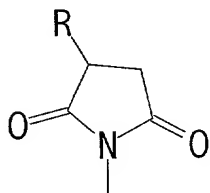
3
4
5 wherein n comprises a whole integer from 1 to 3, R₁ comprises methyl,
6 R₂ comprises polyisobutyl having less than 32 carbon atoms, m comprises a
7 whole integer of from 1 to 3, x comprises a whole integer of from 1 to 20, Int.
8 comprises one or more initiating radicals and Ter. comprises one or more
9 terminating groups. R₁ and R₂ may also comprise methyl and the other of
10 R₁ and R₂ may comprise one or more polyisobutylys having about 5 to about
11 25 carbon atoms. This PIB/UAR copolymer may be liquid at ambient
12 temperature. This PIB/UAR copolymer may be prepared by reacting maleic
13 anhydride with one or more polyisobutenes having less than about 32 carbon
14 atoms, more preferably 28 carbon atoms, in the presence of one or more free
15 radical initiators. This PIB/UAR copolymer may have an average degree of
16 polymerization of about 1.1 to about 20, more preferably about 1.5 to about 10
17 and average molecular weight of about 231 to about 10,920. The
18 polyisobutene used to make this PIB/UAR copolymer may comprise about 5
19 wt. % to about 20 wt. % C₈H₁₆, about 35 wt. % to about 55 wt. % C₁₂H₂₄,
20 about 20 wt. % to about 30 wt. % C₁₆H₃₂, about 8 wt. % to about 15 wt. %
21 C₂₀H₄₀, about 2 wt % to about 8 wt % C₂₄H₄₈, and about 0.5 wt % to about 2
22 wt. % C₂₈H₅₆. The polyisobutene used to make this PIB/UAR copolymer may
23 have a number average molecular weight (M_n) of about 150 to about 240.
24 This PIB/UAR copolymer may be used with polyisobutene having less than
25 about 32 carbon atoms with maleic anhydride in the presence of one or more
26 free radical initiators to make more of this copolymer. This PIB/UAR
27 copolymer may be prepared by performing a first step of reacting a first

1 amount of unsaturated acidic reagent with a first amount of polyisobutene
 2 having less than about 32 carbon atoms, more preferably less than about 28
 3 carbon atoms, in the presence of a first amount of free radical initiator to form
 4 a first liquid PIB/UAR copolymer and a second step of reacting a portion of the
 5 first liquid PIB/UAR copolymer with a second amount of unsaturated acidic
 6 reagent, a second amount of polyisobutene having less than about 32 carbon
 7 atoms, more preferably less than about 28 carbon atoms, in the presence of
 8 a second amount of free radical initiator.

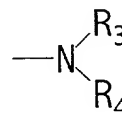
9 This invention may also comprise one or more polymers having the
 10 general formula of:



11
 12 wherein W comprises one or more of :



and



13
 14
 15 wherein R comprises at least one of one or more polyalkyls and one or more
 16 polyalkenes wherein the polyalkyls and polyalkenes each have a molecular
 17 weight of at least 1000; R1 comprises methyl; R2 comprises polyisobutyl
 18 having less than 32 carbon atoms; Z comprises one or more polyamine linking
 19 radicals; m comprises a whole integer of from 1 to 3; n comprises a whole
 20 integer of from 1 to 3; x comprises a whole integer of from 1 to 20; Int.
 21 comprises one or more initiating radicals; Ter. comprises one or more
 22 terminating groups; and wherein R3 and R4 are independently hydrogen,

1 alkyl, phenyl, or taken together are alkylene to give a ring group. This
 2 polymer may be a part of a lubricating oil composition comprising a major
 3 amount of oil of lubricating viscosity and a minor amount of this polymer. This
 4 polymer may also be a part of a lubricating oil concentrate comprising from
 5 about 10 wt. % to about 90 wt. % of this polymer and from about 90 wt. % to
 6 about 10 wt. % of an oil of lubricating viscosity. This polymer may also be a
 7 part of a fuel concentrate comprising a major amount of an inert stable
 8 oleophilic organic solvent boiling in the range of about 150 degrees F. to
 9 about 400 degrees F. and a minor amount of this polymer. This PIB/UAR
 10 copolymer may also be post treated with one or more cyclic carbonates or
 11 one or more linear mono- or poly-carbonates under reactive conditions to form
 12 one or more post-treated dispersants. A preferred cyclic carbonate is ethylene
 13 carbonate. This post-treated dispersant may be a part of a lubricating oil
 14 comprising a minor amount of the post-treated dispersant and a major amount
 15 of an oil of lubricating viscosity. The lubricating oil concentrate may comprise
 16 from about 10 wt. % to about 90 wt. % of this post-treated dispersant and from
 17 90 wt. % to about 10 wt. % of an oil of lubricating viscosity. The polymer may
 18 also be post-treated with one or more of boron oxide, boron halide, boric acid,
 19 and esters of boric acid under reactive conditions to form one or more post-
 20 treated dispersants.

21 A process for preparing one or more succinimides comprising reacting
 22 a mixture under reactive conditions in the presence of one or more free
 23 radical initiators, wherein the mixture comprises one or more of at least one
 24 alkenyl acid derivative and at least one alkylsuccinic acid derivative and one
 25 or more PIB/UAR copolymers prepared by reacting one or more unsaturated
 26 acidic reagents with one or more polyisobutenes having less than about 32
 27 carbon atoms and one or more polyamines. The acid derivative may have a
 28 succination ratio of about from 1.1 to about 1.4. This succinimide may be
 29 prepared by reacting a mixture under reactive conditions wherein the mixture
 30 comprises one or more of an alkenyl acid derivative and an alkylsuccinic acid
 31 derivative, one or more copolymers of one or more unsaturated acidic
 32 reagents and one or more polyisobutenes having less than about 32 carbon
 33 atoms, and one or more polyamines. This succinimide may comprise one or
 34 more acid derivatives that have a succination ratio of about from about 1.1 to

1 about 1.4. The unsaturated acidic reagent may comprise maleic anhydride.
2 This invention may comprise a lubricating oil composition comprising a major
3 amount of an oil of lubricating viscosity and a minor amount of this
4 succinimide, more particularly, about 10 wt. % to about 90 wt. % of this
5 succinimide and from about 90 wt. % to about 10 wt. % of an oil of lubricating
6 viscosity. This invention may comprise one or more fuel concentrates that
7 comprise a major amount of an inert stable oleophilic organic solvent boiling
8 in the range of about 150 degrees F. to about 400 degrees F. and a minor
9 amount of this succinimide.

10 This succinimide may be post-treated with one or more of the following
11 carbonates, linear mono- carbonates and poly-carbonates, under reactive
12 conditions. The carbonates may comprise ethylene carbonate. This invention
13 may comprise a lubricating oil comprising a major amount of an oil of
14 lubricating viscosity and a minor amount of this post-treated succinimide, or
15 more particularly, about 10 wt. % to about 90 wt. % of this post-treated
16 succinimide and from about 90 wt. % to about 10 wt. % of an oil of lubricating
17 viscosity. This invention may also comprise a fuel concentrate comprising a
18 major amount of an inert stable oleophilic organic solvent boiling in the range
19 of about 150 degrees F. to about 400 degrees F. and a minor amount of this
20 post-treated succinimide.

21 This invention may comprise one or more post-treated succinimides
22 prepared by treating succinimides under reactive conditions with a one or
23 more of boron oxide, boron halide, boric acid, and esters of boric acid. The
24 succinimides of this invention may also be post-treated with one or more of
25 boron oxide, boron halide, boric acid, and esters of boric acid. This invention
26 may also comprise lubricating oil comprising a major amount of oil of
27 lubricating viscosity and a minor amount of the succinimide post treated with a
28 boron compound. This invention may comprise a fuel concentrate comprising
29 a major amount of an inert stable oleophilic organic solvent boiling in the
30 range of about 150 degrees F. to about 400 degrees F. and a minor amount
31 of this succinimide that has been post treated with one or more boron
32 compounds.

1

2 **BRIEF DESCRIPTION OF THE DRAWING**

3 To assist the understanding of this invention, reference will be made to
4 the formulas presented throughout and in Fig. 1. The formulas are exemplary
5 only, and should not be construed as limiting the invention.

6 FIG 1 depicts one embodiment of a (1) PIBSA reacted with a
7 (2) PIB/UAR copolymer having a (R) low molecular weight polyisobutyl group
8 in the presence of (3) triethylenetetraamine (TETA) at 165 degrees C. to form
9 a (4) polysuccinimide. This polysuccinimide may be post-treated with
10 (5) cyclic carbonate to yield a (6) post-treated polysuccinimide.

11

12 **DEFINITIONS**

13 As used in this patent application, whether or not capitalized, the
14 following terms have the following meanings unless specifically stated
15 otherwise.

16 The term "PIB" is an abbreviation for polyisobutene.

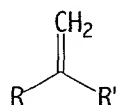
17 The terms "low molecular weight PIB" refers herein to PIBs that
18 comprise less than about 32 carbons atoms.

19 The terms "low molecular weight PIB/UAR copolymer" or "PIB/UAR
20 copolymer" refers to a copolymer prepared using low molecular weight PIB.

21 The term "degree of polymerization" expresses the length of a linear
22 polymer and refers to the number of repeating (monomeric) units in the chain.
23 The number average molecular weight of a polymer is the product of the
24 degree of polymerization and the number average molecular weight of the
25 repeating unit (monomer). Accordingly, the average degree of polymerization
26 is calculated by dividing the number average molecular weight of the polymer
27 by the number average molecular weight of the repeating unit.

28 The term "polysuccinimide" refers to a succinimide comprising the
29 reaction product of a copolymer with an alkyl or alkenyl succinic acylating
30 agent and a polyamine.

1 The term "alkylvinylidene" or "alkylvinylidene isomer" refers to olefins
2 and polyalkylene components having the following vinylidene structure



3 (A)

4 wherein R is polyisobutyl having less than about 29 carbon atoms and R' is
5 lower an alkyl of about 1 to about 6 carbon atoms.

6 The term "chain transfer agent" means an agent that will provide an
7 active hydrogen or halogen that can be abstracted during a polymerization
8 reaction. Chain transfer reactions stop a growing chain radical and start a
9 new one in its place. Thus chain transfer results in shorter chains, lower
10 degree of polymerization and lower molecular weights. Typical chain transfer
11 agents may include mercaptans, aromatic compounds with benzylic
12 hydrogens, halogenated hydrocarbons such as carbon tetrachloride and
13 carbon tetrabromide

14 The term "succinimide" is understood in the art to include many of the
15 amide, imide, etc. species that are also formed by the reaction of a succinic
16 anhydride with an amine. The predominant products, however, are
17 succinimides and this term has been generally accepted as meaning the
18 product of a reaction of alkenyl- or alkyl-substituted succinic acid or
19 anhydride with polyamine. Alkenyl or alkyl succinimides are disclosed in
20 numerous references and are well known in the art. Certain fundamental
21 types of succinimides and related materials encompassed by the term of art
22 "succinimide" are taught in U.S. Patent Nos. 2,992,708; 3,018,291; 3,024,237;
23 3,100,673; 3,219,666; 3,172,892; and 3,272,746, the disclosures of which are
24 hereby incorporated by reference.

25 The term "Total Base Number" or "TBN" refers to the amount of base
26 equivalent to milligrams of KOH in 1 gram of sample. Thus, higher TBN
27 numbers reflect more alkaline products and therefore a greater alkalinity
28 reserve. The TBN of a sample may be determined by ASTM Test No. D2896
29 or any other equivalent procedure.

The term "SAP" refers to Saponification Number and may be determined by the procedure described in ASTM D94 or any other equivalent procedure.

The term "TAN" refers to Total Acid Number and may be determined by the procedure described in ASTM D 664 or any other equivalent procedure.

The "succinic ratio" may be calculated from the saponification number (mg KOH per gram of sample), the actives content of the alkenyl or alkyl succinic anhydride product and the molecular weight of the starting polyolefin. The actives content of the alkenyl or alkyl succinic anhydride product is measured in terms of the actives fraction, wherein an actives fraction of 1.0 is equivalent to 100 weight percent actives. Accordingly, an actives fraction of 0.5 would correspond to 50 weight percent actives.

The succinic ratio of the alkenyl or alkyl succinic anhydride product of maleic anhydride and polyolefin can be calculated in accordance with the following equation:

$$\text{Succinic ratio} = \frac{M_{po} \times P}{(C \times A) - (M_{ma} \times P)}$$

wherein

P = saponification number of the alkenyl or alkyl succinic anhydride sample (mg KOH/g)

A = actives fraction of the alkenyl or alkyl succinic anhydride sample

M_{po} = number average molecular weight of the starting polyolefin

M_{ma}=98 (molecular weight of maleic anhydride)

C = conversion factor=112220 (for conversion of gram-moles of alkenyl or alkyl succinic anhydride per gram of sample to milligrams of KOH per gram of sample).

The actives fraction of the alkenyl or alkyl succinic anhydride may be determined from the percent of unreacted polyolefin according to the following procedure. A 5.0 gram sample of the reaction product of maleic anhydride and polyolefin is dissolved in hexane, placed in a column of 80.0 grams of silica gel (Davisil 62, a 140 angstrom pore size silica gel), and eluted with 1 liter of hexane. The percent unreacted polyolefin is determined by removing

the hexane solvent under vacuum from the eluent and weighing the residue.

Percent unreacted polyolefin is calculated according to the following formula:

$$\text{Percent Unreacted Polyolefin} = \frac{\text{Net Weight of Residue}}{\text{Sample Weight}} \times 100$$

The weight percent actives for the alkenyl or alkyl succinic anhydride product is calculated from the percent unreacted polyolefin using the formula:

$$\text{Weight Percent Actives} = 100 - \text{Percent Unreacted Polyolefin}$$

The actives fraction of the alkenyl or alkyl succinic anhydride is then calculated as follows:

$$\text{Actives Fraction} = \frac{\text{Weight Percent Actives}}{100}$$

The percent conversion of polyolefin is calculated from the weight percent actives as follows:

Percent Conversion =

$$\frac{\text{wt. \% actives} \times \left(\frac{M_{po}}{M_{po} + [M_{ma} \times SR]} \right)}{\left[\text{wt. \% actives} \times \left(\frac{M_{po}}{M_{po} + [M_{ma} \times SR]} \right) \right] + [100 - \text{wt. \% actives}]}$$

1 wherein

2 M_{po} = number of average molecular weight of the starting polyolefin

3 M_{ma} = 98(molecular weight of maleic anhydride)

4 SR = succinic ratio of alkenyl or alkyl succinic anhydride product

5 It is, of course, understood that alkenyl or alkyl succinic anhydride
6 products having high succinic ratios can be blended with other alkenyl
7 succinic anhydrides having lower succinic ratios, for example ratios of around
8 1.0, to provide an alkenyl succinic anhydride product having an intermediate
9 succinic ratio.

10 In general, suitable succinic ratios for the alkenyl or alkyl succinic
11 anhydride reactants employed in preparing the additives of this invention are
12 greater than about 1 but less than about 2. Succinic anhydrides with succinic
13 ratios of about 2, when reacted with amines having greater than 4 nitrogen
14 atoms per mole and post-treated with a cyclic carbonate, form gels.
15 Accordingly, succinic ratios of about 1.7 or less are preferred.

16

17 **DETAILED DESCRIPTION OF THE INVENTION**

18 **A. THE PIB/UAR COPOLYMER**

19 One embodiment of this invention is a copolymer referred to herein as
20 the PIB/UAR copolymer. The PIB/UAR copolymer may be prepared by
21 reacting a low molecular weight PIB with an unsaturated acidic reagent in the
22 presence of a free radical initiator.

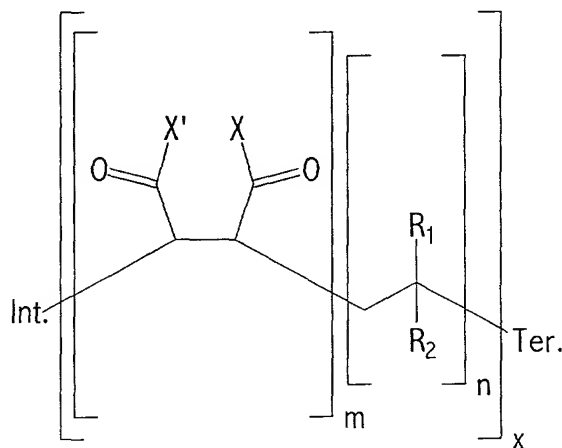
23 Preferred PIB/UAR copolymers include those in which an unsaturated
24 acidic reagent, most preferably maleic anhydride, is copolymerized with a low
25 molecular weight PIB and wherein about 20 % or more, preferably about 50 %
26 or more, and more preferred about 80 % or more of the olefinic bonds of the
27 PIB comprises alkylvinylidene.

28 More preferred PIB/UAR copolymers include those in which an
29 unsaturated acidic reagent, most preferably maleic anhydride, is
30 copolymerized with a low molecular weight PIB wherein about 20 % or more,
31 preferably about 50 % or more, and more preferred about 80 % or more of the
32 olefinic bonds of the PIB comprises methylvinylidene.

1 PIB/UAR copolymers may comprise a mixture of low molecular weight
 2 PIB molecules of varying molecular weight because low molecular weight
 3 PIB used to prepare PIB/UAR copolymers are generally mixtures of individual
 4 molecules of different molecular weights. Also, the PIB/UAR copolymer may
 5 comprise PIB/UAR copolymer molecules having different degrees of
 6 polymerization.

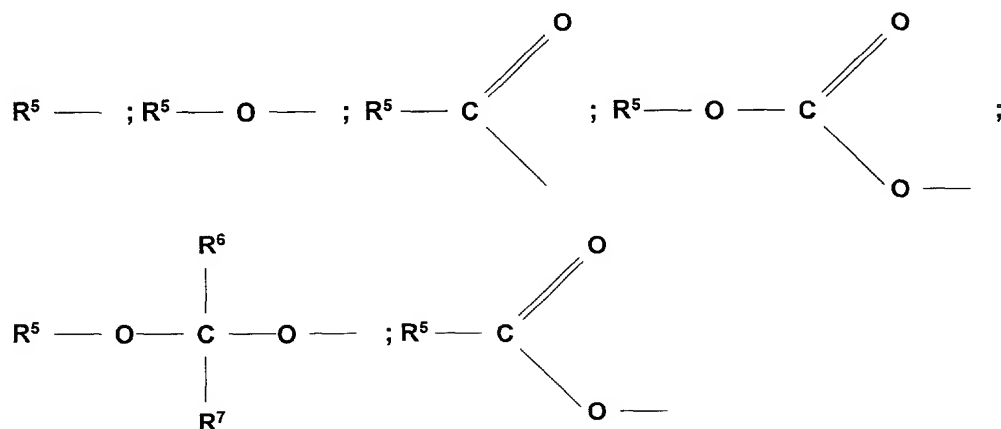
7 The PIB/UAR copolymers have an average degree of polymerization of
 8 about 1.1 to about 20, and more preferably from about 1.5 to about 10. The
 9 PIB/UAR copolymers have a number average molecular weight of about
 10 231 to about 10,920. Among other factors, the present invention is based on
 11 the surprising finding that the preparation of the PIB/UAR copolymer does not
 12 require the use of any chain transfer agents and the PIB/UAR copolymer is
 13 liquid at ambient temperatures. Thus, the PIB/UAR copolymers are prepared
 14 by reacting a low molecular weight PIB in which a high proportion of
 15 unsaturation, about 20% or more is in the alkylvinylidene configuration, with
 16 an unsaturated acidic reagent in the presence of a free radical initiator.

17 The succinic ratio of the PIB/UAR copolymer may be greater than 1 or
 18 less than 1. The PIB/UAR copolymer may be alternating or random. The
 19 PIB/UAR copolymers may have the general formula:



(C)

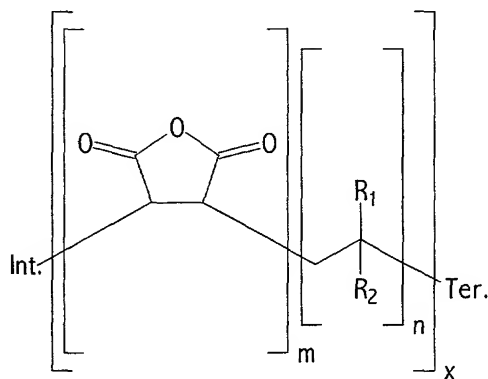
1 wherein:
2 X and X' comprise one or more of —OH; —O—hydrocarbyl; —NH₂; —Cl;
3 —Br; —OM⁺, wherein M⁺ comprises one equivalent of one or more
4 metals, ammoniums or amine cations; and X and X' take together as
5 —O— so as to form an anhydride;
6 n is a whole integer from 1 to 3;
7 R₁ comprises methyl;
8 R₂ comprises polyisobutyl having less than 32 carbon atoms, preferably about
9 5 to about 25 carbon atoms;
10 m comprises a whole integer of from 1 to 3;
11 x comprises a whole integer of from 1 to 20, preferably about 2 to about 10,
12 more preferably 2 to 8;
13 Int. comprises one or more initiating radicals; and
14 Ter. comprises one or more terminating groups.
15 The Int. and Ter. substituents are a result of the free radical initiator
16 used to prepare the PIB/UAR copolymer. Typical (Int.) and (Ter.) groups may
17 include:



(D)

18 wherein R⁵ is hydrogen, alkyl, aryl, alkaryl, cycloalkyl, alkoxy, cycloalkoxy,
19 acyl, alkenyl, cycloalkenyl, alkynyl; or alkyl, aryl or alkaryl optionally
20 substituted with 1 to 4 substituents independently selected from nitrile, keto,
21 halogen, nitro, alkyl, aryl, and the like; and R⁶ and R⁷ are independently
22 hydrogen, alkyl, aryl, alkaryl, and the like.

1 In a preferred embodiment, when maleic anhydride is used as the
 2 unsaturated acidic reagent, the reaction produces PIB/UAR copolymers
 3 predominately of the following formula:
 4
 5



6
 7
 8 wherein R_1 , R_2 , n , m , x , Int. and Ter. are as defined in formula (C).
 9

10 **A(1) LOW MOLECULAR WEIGHT POLYISOBUTENE (PIB)**

11 Preferred low molecular weight PIBs comprise less than about
 12 32 carbon atoms, for example, one or more of 32 carbon atoms, 28 carbon
 13 atoms, 24 carbon atoms, 20 carbon atoms, 16 carbon atoms, 12 carbon
 14 atoms, and 8 carbon atoms. More preferred low molecular weight PIBs
 15 comprise from about 8 to about 28 carbon atoms. Most preferred low
 16 molecular weight PIBs comprise from about 12 to about 28 carbon atoms.
 17 Preferred low molecular weight PIBs have a molecular weight of about 448 or
 18 less. More preferred low molecular weight PIBs have a molecular weight of
 19 about 112 to about 392. Most preferred low molecular weight PIB has a
 20 molecular weight of about 168 to about 392.

21 The PIBs of this invention may be mixtures of individual low molecular
 22 weight PIB molecules of varying molecular weights. A mixture of low
 23 molecular weight PIBs might comprise any or all of C_8 , C_{12} , C_{16} , C_{20} , C_{24} , C_{28}
 24 and C_{32} molecules. One embodiment of this invention may comprise the use
 25 of low molecular weight PIB molecules that have been separated according to
 26 carbon number. For example, a PIB mixture may be distilled to provide
 27 compositions that comprise one or more of C_8 , C_{12} , C_{16} , C_{20} , C_{24} , C_{28} , or C_{32}

1 molecules. Preferred low molecular weight PIBs of this invention are those
2 that are used as a mixture of varying molecular weights. A preferred low
3 molecular weight PIB mixture may have the M_n of about 150 to about 240.

4 A preferred low molecular weight PIB mixture may comprise the
5 following: about 5 wt. % to about 20 wt. % C_8H_{16} , about 35 wt. % to about
6 55 wt. % $C_{12}H_{24}$, about 20 wt. % to about 30 wt. % $C_{16}H_{32}$, about 8 wt. % to
7 about 15 wt. % $C_{20}H_{40}$, about 2 wt % to about 8 wt % $C_{24}H_{48}$, and about 0.5 wt
8 % to about 2 wt % $C_{28}H_{56}$. $C_{32}H_{64}$ and higher species may comprise about
9 2 wt % or less of the total.

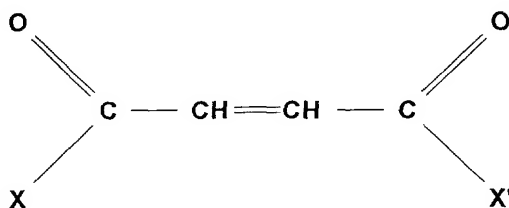
10 The olefinic bonds of a preferred low molecular weight PIB may
11 comprise about 20 % or more, preferably about 50 % or more, and more
12 preferred about 80 % or more of the alkylvinylidene isomer.

13 The olefinic bonds of a more preferred low molecular weight PIB may
14 comprise about 20 % or more, preferably about 50 % or more, and more
15 preferred about 80 % or more of the methylvinylidene isomer.

16 Preferred PIBs include those PIBs prepared using a boron trifluoride
17 (BF_3) catalyst. The preparation of PIBs in which the methylvinylidene isomer
18 comprises a high percentage of the total composition is described in U.S. Pat.
19 Nos. 4,152,499 and 4,605,808. Low molecular weight PIB may be prepared
20 directly or they may be a distilled fraction of higher molecular weight
21 polybutene.

22 23 **A(2) UNSATURATED ACIDIC REAGENT**

24 The term "unsaturated acidic reagent" refers to maleic or fumaric
25 reagents of the general formula:



(G)

26 wherein X and X' are the same or different, provided that at least one of X and
27
28 X' is a group that is capable of reacting to esterify alcohols, form amides, or
29

1 amine salts with ammonia or amines, form metal salts with reactive metals or
2 basically reacting metal compounds and otherwise function as acylating
3 agents. Typically, X and X' comprise functional groups that may comprise one
4 or more of —OH; —O—hydrocarbyl; —OM⁺ when M⁺ represents one
5 equivalent of a metal, ammonium, or amine cation; —NH₂; —Cl; —Br; or
6 taken together X and X' may be —O— so as to form an anhydride. Preferably,
7 X and X' are such that both carboxylic functions can enter into acylation
8 reactions. Maleic anhydride is a preferred unsaturated acidic reagent. Other
9 suitable unsaturated acidic reagents include electron-deficient olefins such as
10 monophenyl maleic anhydride; monomethyl, dimethyl, monochloro,
11 monobromo, monofluoro, dichloro and difluoro maleic anhydride, N-phenyl
12 maleimide and other substituted maleimides; isomaleimides; fumaric acid,
13 maleic acid, alkyl hydrogen maleates and fumarates, dialkyl fumarates and
14 maleates, fumaronilic acids and maleanic acids; and maleonitrile, and
15 fumaronitrile.

17 **A(3) FREE RADICAL INITIATOR**

18 A free radical initiator is a molecular fragment having one or more
19 unpaired electrons that are capable of initiating a polymerization reaction.
20 Any free radical initiator may initiate the copolymerization described herein.
21 Such initiators are well known in the art. However, the choice of free radical
22 initiator may be influenced by the reaction temperature used.

23 The preferred free radical initiators are the peroxide-type
24 polymerization initiators and the azo-type polymerization initiators. Radiation
25 may also be used to initiate the reaction, if desired.

26 The peroxide-type free radical initiator may be organic or inorganic.
27 Organic free radical initiators may have the general formula: ROOR' wherein
28 R comprises any organic radical and R' comprises one or more of hydrogen
29 and any organic radical. Both R and R' may be organic radicals, preferably
30 hydrocarbon, aroyl, and acyl radicals, carrying, if desired, substituents such
31 as halogens. Preferred peroxides include di-tert-butyl peroxide, tert-butyl
32 peroxybenzoate, and dicumyl peroxide.

33 Examples of other suitable peroxides, which in no way are limiting,
34 include benzoyl peroxide; lauroyl peroxide; other tertiary butyl peroxides;

1 2,4-dichlorobenzoyl peroxide; tertiary butyl hydroperoxide; cumene
2 hydroperoxide; diacetyl peroxide; acetyl hydroperoxide;
3 diethylperoxycarbonate; tertiary butyl perbenzoate; and the like.

4 The azo-type compounds, typified by
5 alpha,alpha'-azobisisobutyronitrile, are also well-known free radical promoting
6 materials. These azo compounds may be defined as those having present in
7 the molecule group $-N=N-$ wherein organic radicals satisfy the balance, at
8 least one of which is preferably attached to a tertiary carbon. Other suitable
9 azo compounds include, but are not limited to, p-bromobenzenediazonium
10 fluoborate; p-tolyldiazoaminobenzene; p-bromobenzenediazonium hydroxide;
11 azomethane and phenyldiazonium halides. A suitable list of azo-type
12 compounds may be found in U.S. Pat. No. 2,551,813, issued May 8, 1951 to
13 Paul Pinkney.

14 The amount of free radical initiator to employ, exclusive of radiation,
15 depends to a large extent on the particular initiator selected, the low molecular
16 PIB used and the reaction conditions. A preferred initiator is one that is
17 soluble in the reaction medium. Preferred concentrations of initiator may be
18 between about 0.001:1 and about 0.2:1 moles of initiator per mole of acidic
19 reagent, with preferred amounts between about 0.005:1 and about
20 0.10:1 moles.

21 It is preferred that the polymerization temperature is sufficiently high to
22 break down the free radical initiator to produce the desired free radical s. The
23 half-life values for known free radical initiators at various temperatures are
24 readily available from the literature. See, for example, C. Walling,
25 "Free Radicals in Solution", John Wiley and Sons, Inc., New York (1957).
26 Alternatively, the half-life values are available from the various suppliers of
27 free radical initiators. Table 1 lists the half-life temperatures for a number of
28 free radical initiators at a given half-life. The half-life temperature is the
29 temperature required for a free radical initiator to exhibit a specified half-life.
30 As a rule, the higher the half-life temperature, the lower the half-life of the free
31 radical initiator.

Table 1

HALF-LIFE TEMPERATURES OF VARIOUS FREE
RADICAL INITIATORS AT SPECIFIED HALF-LIVES

Free Radical Initiators	Half-Life (Temperature in degrees C.)				
	5 Min.	10 Min.	2 Hrs.	5 Hrs.	10 Hrs.
Dialkyl Peroxides: di-t-butyl peroxide	173	166	143	135	129
di-t-amyl peroxide	167	160	137	129	123
di-cumyl peroxide	161	154	131	123	117
2, 5-dimethyl-2,	164	157	134	126	120
5-di(t-butylperoxy) hexane Peroxyketals: 1, 1-di-tannylperoxy-	134	128	106	99	93
Cyclohexane Diperoxycarbonates: di-ethylhexylperoxy-	85	79	60	54	49
Dicarbonate Diacyl Peroxides: didecanoyl peroxide	102	96	76	69	64

In carrying out the process of the invention, a single free radical initiator or a mixture of free radical initiators may be employed. For example, it may be desirable to add an initiator having a low decomposition temperature as the mixture is warming to reaction temperature, and then add an initiator having a higher decomposition temperature as the mixture reaches higher reaction temperatures. Alternatively, a combination of initiators could both be added prior to heating and reaction. In this case, an initiator having a high decomposition temperature would initially be inert, but would later become active as the temperature rose.

The initiator may also be added over time. For example, if an initiator is chosen with a short half-life, e.g., 5-20 minutes, at the reaction temperature, then the initiator may be added over a period of time so that an adequate concentration of free radicals will be available throughout the reaction period to give improved yields of the desired product.

1 **A(4) GENERAL PREPARATION OF PIB/UAR COPOLYMER**

2 The PIB/UAR copolymers may be prepared by reacting a low
3 molecular weight PIB with an unsaturated acidic reagent in the presence of a
4 free radical initiator.

5 The reaction may be conducted neat, that is, the low molecular weight
6 PIB, the unsaturated acidic reagent and the free radical initiator are combined
7 in the proper ratio, and then stirred at the reaction temperature.

8 The reaction time is usually sufficient to result in the substantially
9 complete conversion of the reactive isomers of the low molecular weight PIB
10 to the PIB/UAR copolymer. Suitable reaction times may be between one and
11 24 hours, with preferred reaction times between two and ten hours.

12 The low molecular weight PIB, unsaturated acidic reagent, and free
13 radical initiator may be brought together in any suitable manner. No solvent
14 is required. The important factors are intimate contact of the low molecular
15 weight PIB and unsaturated acidic reagent in the presence of a free radical
16 agent. The reaction, for example, may be conducted in a batch system in
17 which the low molecular weight PIB is added all initially to a mixture of
18 unsaturated acidic reagent and free radical initiator. The low molecular weight
19 PIB may also be added intermittently or continuously to the other reactants.
20 Alternatively, the reagents may be combined in other orders; for example, the
21 unsaturated acidic reagent and free radical initiator may be added to low
22 molecular weight PIB. The components in the reaction mixture may also be
23 added continuously to a stirred reactor with continuous removal of a portion of
24 the product to a recovery train or to other reactors in series. The reaction may
25 also take place in a tubular reactor in which the components may be added at
26 one or more points along the tube.

27 The reaction may be conducted at a temperature of about -
28 30 degrees C. to about 210 degrees C., preferably from about 40 degrees C.
29 to about 150 degrees C. As noted in the section regarding free radical
30 initiators, it is preferred that the polymerization temperature is sufficiently high
31 to decompose the free radical initiator to produce the desired free radicals.
32 For example, using benzoyl peroxide as the initiator, the reaction temperature
33 may be between about 75 degrees C. and about 90 degrees C., preferably
34 between about 80 degrees C. and about 85 degrees C. The degree of

1 polymerization is inversely proportional to the temperature. Thus, higher
2 reaction temperatures are preferred for preparing PIB/UAR copolymers with a
3 particularly low degree of polymerization. In general, after the reaction is
4 deemed complete, for example, by NMR analysis, the reaction mixture is
5 heated to decompose any residual initiator. For a di-tert-butyl peroxide
6 initiator, this temperature is typically about 160 degrees C. or higher.

7 When the low molecular weight PIB, the unsaturated acidic reagent
8 and the free radical initiator react to form PIB/UAR copolymer, the PIB/UAR
9 copolymer that is formed helps dissolve the unsaturated acidic reagent. This
10 phenomenon facilitates the reaction of unreacted low molecular weight PIB,
11 unsaturated acidic reagent and free radical initiator. In light of this
12 phenomenon, previously formed PIB/UAR copolymer may be used to facilitate
13 new reactions of low molecular weight PIB, unsaturated acidic reagent and
14 free radical initiator reactants. Using the PIB/UAR copolymer to facilitate this
15 reaction is referred to herein as the heel process.

16 A preferred method to use the PIB/UAR copolymer in the heel process
17 is to combine the low molecular weight PIB, the unsaturated acidic reagent
18 and PIB/UAR copolymer; heat this combination to reaction temperature; and
19 then add the free radical initiator while maintaining a suitable reaction
20 temperature. This process may be conducted in batch or in continuous mode.

21 The PIB/UAR copolymer for use the heel process may be obtained by
22 retaining a portion of the PIB/UAR copolymer from a previous run. Preferred
23 PIB/UAR copolymers for use in the heel process include the copolymer
24 product of maleic anhydride and low molecular weight PIB. The preferred
25 volume ratio of PIB/UAR copolymer to low molecular weight PIB in the heel
26 process is between 1:1 and 1:100. A more preferred volume ratio of PIB/UAR
27 copolymer to low molecular weight PIB in the heel process is between
28 1:1.5 and 1:4.

29 The heel process reaction may be conducted at a preferred
30 temperature in the range of about 90 degrees C. to about 210 degrees C.,
31 and more preferably from about 130 degrees C. to about 150 degrees C. At
32 lower reaction temperatures the reaction mixture may become too viscous
33 and may require a solvent to obtain satisfactory reaction.

1 The heel process reaction may be used in a batch process or a
2 continuous process. The reaction temperature range may be about
3 90 degrees C. to 210 degrees C. and preferably about 130 degrees C. to
4 150 degrees C. The unsaturated acidic reagent charge may theoretically
5 range from 1 to 2 moles of unsaturated acidic reagent per mole of methyl
6 vinylidene isomer of PIB. Typically, the free radical initiator may be charged at
7 about 0.1 moles initiator per about 1.0 moles unsaturated acidic reagent,
8 although this may vary. The reaction may be carried out at atmospheric
9 pressure. At higher temperatures, it may be desirable to pressurize the
10 reactor slightly (i.e., 10 psig) to suppress the loss of unsaturated acidic
11 reagent to the vapor phase.

12 If a batch reaction is used, PIB/UAR copolymer from a previous run
13 and low molecular weight PIB may be charged to the reactor. A sufficient ratio
14 of low molecular weight PIB to PIB/UAR copolymer to assure complete
15 solubility of unsaturated acidic reagent in the mixture at reaction conditions is
16 preferred. If PIB/UAR copolymer is not added at a sufficient level so as to
17 maintain total unsaturated acidic reagent solubility, the rate of reaction may be
18 negatively affected, and the formation of resin may be likely. To maximize
19 reactor productivity, the minimum amount of PIB/UAR copolymer that is
20 optimal to maintain total solubility of the unsaturated acidic reagent charge
21 should be used. The reactor may be stirred and heated to the desired reaction
22 temperature, and the unsaturated acidic reagent and free radical initiator may
23 be added at the appropriate time/times during this step. Reaction times will
24 vary with temperature, concentration of reactants, and types of free radical
25 initiators. When the reaction is complete, removal of any unreacted
26 unsaturated acidic reagent may be accomplished by increasing the reactor
27 temperature to about 150 degrees C. to about 250 degrees C., preferably
28 about 180 degrees C. to about 200 degrees C., while applying sufficient
29 vacuum. This procedure also tends to decompose any remaining free radical
30 initiator.

31 If the reaction is run continuously, a continuous stirred tank reactor
32 (CSTR) or series of such reactors may be used. PIB, unsaturated acidic
33 reagent, and free radical initiator may be fed continuously at appropriate
34 rates so as to maintain a certain level of conversion of the reactants to

1 PIB/UAR copolymer. It is envisioned that the product stream from the reactor
2 then is heated to a temperature in the range of about 150 degrees C. to about
3 250 degrees C. and preferably in the range from about 180 degrees C. to
4 about 200 degrees C. to strip off any unreacted unsaturated acidic reagent
5 and to decompose any remaining free radical initiator. Vacuum may also be
6 used to facilitate removing any unreacted unsaturated acidic reagent. It is
7 envisioned that a wiped film evaporator or similar types of equipment may be
8 suitable for this type of operation.

9 In general, after the reaction is deemed complete, for example, by
10 NMR analysis, the reaction mixture is heated to decompose any residual
11 initiator. For a di-tert-butyl peroxide initiator, this temperature is typically about
12 160 degrees C.

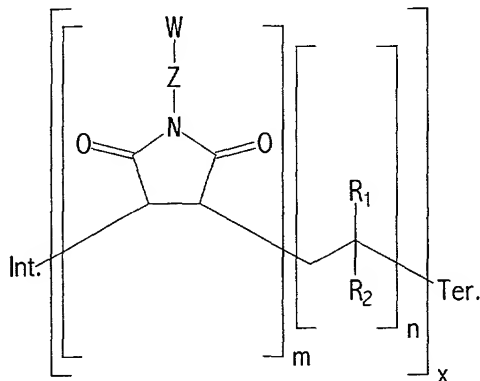
13 Using diluent is not necessary to prepare the PIB/UAR copolymer but
14 one may be used if desired. When diluent is employed, those diluents that are
15 inert to the reactants and products formed are preferred.

16 Using a solvent is not necessary to prepare the PIB/UAR copolymer,
17 but one may be used if desired. When a solvent is employed, solvents that
18 are inert to the reactants and products formed are preferred. Suitable
19 solvents may include acetone, tetrahydrofuran, chloroform, methylene
20 chloride, dichloroethane, toluene, dioxane, chlorobenzene, xylenes, or the
21 like. Solvents may be removed after their usefulness is no longer required.
22 The PIB/UAR copolymer product may be conveniently separated from any
23 solvent used and any unreacted acidic reagent by conventional procedures
24 such as phase separation, solvent distillation, precipitation and the like.
25 Though not required, dispersing agents and/or co-solvents may be used
26 during the reaction if desired.

27 Using a chain transfer agent to prepare the PIB/UAR copolymer of this
28 invention is not required. A chain transfer agent, however, may be used if
29 desired. When a chain transfer agent is employed, chain transfer agents that
30 are inert to the reactants and products formed are preferred.

1 B. POLYSUCCINIMIDES

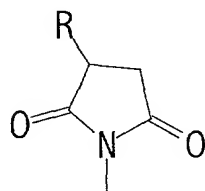
2 One embodiment of this invention is a polymer that may be referred to
 3 herein as a PIB/UAR copolymer succinimide. This polymer is a
 4 polysuccinimide and may be depicted as the general formula:



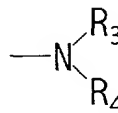
(H)

8 wherein:

9 W comprises one or more of:



and



(I)

12 R comprises at least one of:

13 one or more polyalkyls and one or more polyalkylenes, each of which
 14 have a number average molecular weight of at least about 1000,
 15 preferably from about 1800 to about 3,000;

16 R₁ comprises methyl;

17 R₂ comprises polyisobutyl having less than 32 carbon atoms, preferably about
 18 5 to about 25 carbon atoms;

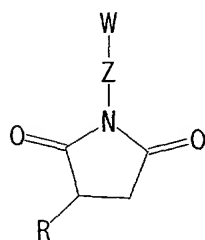
19 Z comprises one or more polyamine linking radicals;

20 m comprises a whole integer of from 1 to 3;

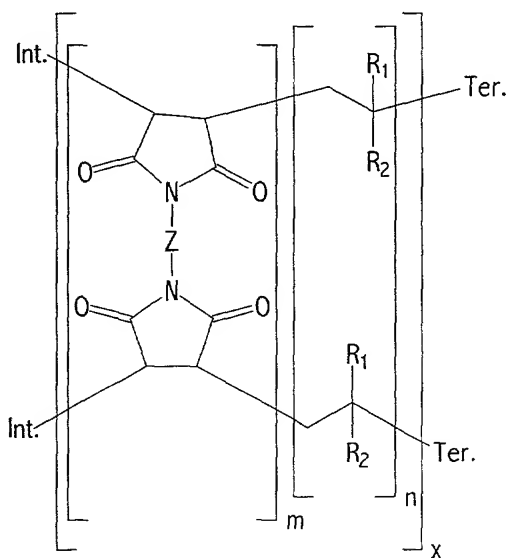
21 n comprises a whole integer of from 1 to 3;

1 x comprises a whole integer of from 1 to 20, preferably about 2 to about 10,
 2 more preferably 2 to 8;
 3 Int. comprises one or more initiating radicals;
 4 Ter. comprises one or more terminating groups; and
 5 wherein R_3 and R_4 are independently hydrogen, alkyl, phenyl, or taken
 6 together are alkylene to give a ring group.

7 The compound of formula (H) may be considered a PIB/UAR
 8 copolymer succinimide and is produced by the reaction of a PIB/UAR
 9 copolymer with a monomer (the alkene or alkyl succinic acid derivative) in
 10 which the monomer is linked to the polymer units by a polyamine linking
 11 radical. Because the PIB/UAR copolymer succinimide mixture may contain
 12 about from 0.5 to 10 equivalents of alkenyl or alkylsuccinic acid derivative
 13 per equivalent of PIB/UAR copolymer, and about from 0.4 to 1.0 equivalents
 14 of polyamine per equivalent of alkenyl or alkylsuccinic acid derivative plus
 15 PIB/UAR copolymer, other structures, such as those presented in
 16 formulas (J) and (K) may also be present, depending on the ratios of alkenyl
 17 or alkylsuccinic acid derivative, PIB/UAR copolymer and polyamine.



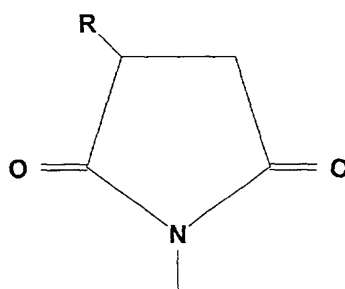
(J)



(K)

18
 19
 20 wherein W, R, R_1 , and R_2 , Z, m, n, x, Int., Ter are the same as described in
 21 formula (H). For example, if the ratio of alkenyl or alkyl succinic acid
 22 derivative per equivalent of unsaturated acidic reagent copolymer is 1.0:1,
 23 and the ratio of polyamine to the sum of the alkenyl or alkylsuccinic acid

1 derivative plus unsaturated acidic reagent copolymer is 0.5:1, then structure
2 (H) would predominate. However, if the ratio of alkenyl or alkylsuccinic acid
3 derivative per equivalent of PIB/UAR copolymer is greater than 1:1, and the
4 ratio of polyamine per equivalent of alkenyl or alkylsuccinic acid derivative
5 plus unsaturated acidic reagent copolymer is 0.5:1, then structures (J) and (K)
6 will predominate, when W is



(L)

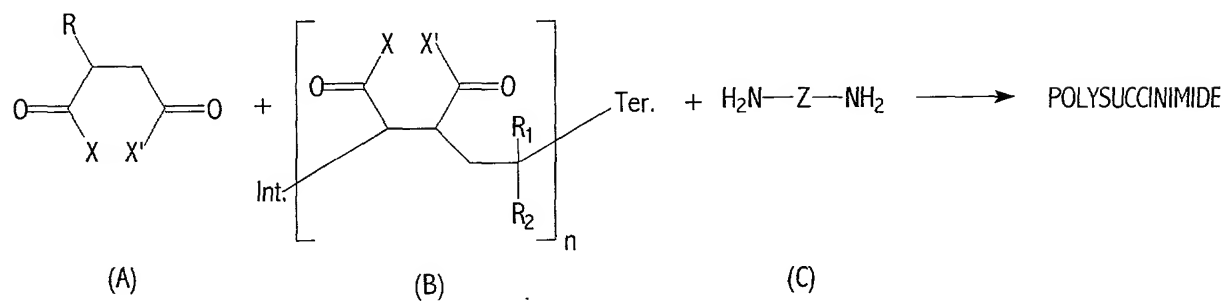
7
8
9 In addition, if the ratio of alkenyl or alkylsuccinic acid derivative
10 per equivalent of PIB/UAR copolymer is greater than 1:1 and the ratio of
11 polyamine to alkenyl or alkylsuccinic acid derivative plus PIB/UAR copolymer
12 is about 1.0:1, then structures (H) and (K) would predominate, when W is
13 NH_2 .

14 In addition to the predominant polymer of formula (H), (J), or (K), the
15 reaction will typically contain more complex reaction products and polymers
16 because of competing and sequential reactions, and because the alkenyl or
17 alkylsuccinic acid derivative might contain more than one succinic anhydride
18 moiety per long chain alkyl or alkenyl group or contain unsaturated acidic
19 reagent oligomers.

20 Referring to formulas (H), (J), or (K), the preferred compounds or
21 compound mixtures are those wherein R is a PIB having an Mn of between
22 1800 and 3000; R_1 is a methyl, R_2 is a low molecular weight PIB; Z is a
23 polyamino radical having about from 3 to 7, more preferably, about
24 4 to 5 nitrogen atoms and 8 to 20 carbon atoms; and x is a whole integer of
25 from 2 through 20.

B(1) SYNTHESIS OF THE POLYSUCCINIMIDE

A succinimide composition comprising PIB/UAR copolymer succinimides may be prepared by contacting the desired alkyl or alkenyl succinic acid derivative with a PIB/UAR copolymer and polyamine under reactive conditions:



(M)

wherein R, R₁, R₂, Z, X, X', n, (Int) and (Ter) are as defined herein.

This process is typically conducted by contacting from about 0.5 to about 10 equivalents of alkenyl or alkylsuccinic acid derivative (reactant A of reaction (M)) per mole of PIB/UAR copolymer (reactant B of reaction (M)) and from about 0.4 to about 1.0 equivalents of amine (reactant C of reaction (M)) per equivalent of alkenyl or alkylsuccinic acid derivative (reactant A of reaction (M)) plus PIB/UAR copolymer (reactant B of reaction (M)). A preferred method is to first add the alkenyl or alkylsuccinic acid derivative and the PIB/UAR copolymer together and then add the polyamine.

A more preferred method is to first mix the alkenyl or alkylsuccinic acid derivative and the PIB/UAR copolymer together using a ratio-controlled mixing system in which these two components are simultaneously charged into a mixing device, such as a static mixer, at the desired weight or mole ratio. In like manner, the alkenyl or alkylsuccinic acid derivative and the PIB/UAR copolymer mixture is then combined with the polyamine using a ratio-controlled mixing system in which these two components are simultaneously charged into a mixing device, such as a static mixer, at the desired weight or mole ratio.

Typically, the reaction is conducted at temperatures in the range of about from about 140 degrees C. to about 180 degrees C., preferably about 150 degrees C. to about 170 degrees C. for about from 1 to 10 hours, preferably 4 to 6 hours. Typically the reaction is conducted at about atmospheric pressure; however, higher or lower pressures can also be used depending on the reaction temperature desired and the boiling point of the reactants or solvent if a solvent is used.

As noted herein, the reaction will typically be a mixture because there are secondary products or byproducts and the reactants are mixtures. In theory, pure compounds could be obtained, for example by using pure compounds as reactants and then separating out the desired pure compounds from the reaction product. However, the expense of this would rarely be justified for commercial purposes and accordingly the commercial product will generally be a mixture in which formulas (H), (J), and (K) will be the predominant compounds.

Water, present in the system or generated by the reaction of the amine with the succinic or maleic anhydride moieties of (reactant A of reaction (M)) and (reactant B of reaction (M)) alkyl succinimide, is preferably removed from the reaction system during the course of the reaction via azeotroping, stripping with nitrogen or distillation. After reaction completion, the system may be stripped at elevated temperatures (typically 100 degrees C. to 250 degrees C.) and reduced pressures to remove any volatile components that may be present in the product.

(B)(1)(A) THE ALKENYL OR ALKYL SUCCINIC ACID DERIVATIVES

Alkyl and alkenylsuccinic acid derivatives having a calculated succinic ratio of from about 1:1 to about 2.5:1, and preferably from about 1:1 to about 1.5:1, may be used in the present process. More preferably, the alkyl or alkenyl succinic acid derivatives have a succination ratio of about from about 1.1 to about 1.4. Most preferably alkyl or alkenylsuccinic anhydrides are used. Accordingly, alkenyl succinic anhydride prepared by the thermal process is preferred, because the calculated succination ratio of material prepared by this process is typically 1.0 to 1.4, and because the product is essentially chlorine-free since chlorine is not used in the synthesis.

1 The polyalkylene succinic anhydride is the reaction product of a
2 polyalkylene (preferably polyisobutene) with maleic anhydride. Conventional
3 polyisobutene, or high methylvinylidene polyisobutene may be used in the
4 preparation of such polyalkylene succinic anhydrides. Thermal, chlorination,
5 free radical, acid catalyzed, or any other process may be used in this
6 preparation. Examples of suitable polyalkylene succinic anhydrides are
7 thermal PIBSA (polyisobutenyl succinic anhydride) described in U.S. Patent
8 No. 3,361,673; chlorination PIBSA described in U.S. Patent No. 3,172,892; a
9 mixture of thermal and chlorination PIBSA described in U.S. Patent No.
10 3,912,764; high succinic ratio PIBSA described in U.S. Patent No. 4,234,435;
11 PolyPIBSA described in U.S. Patent Nos. 5,112,507 and 5,175,225;
12 high succinic ratio PolyPIBSA described in U.S. Patent Nos. 5,565,528 and
13 5,616,668; free radical PIBSA described in U.S. Patent Nos. 5,286,799,
14 5,319,030, and 5,625,004; PIBSA made from high methylvinylidene
15 polybutene described in U.S. Patent Nos. 4,152,499, 5,137,978, and
16 5,137,980; high succinic ratio PIBSA made from high methylvinylidene
17 polybutene described in European Patent Application Publication
18 No. EP 355 895; terpolymer PIBSA described in U.S. Patent No. 5,792,729;
19 sulfonic acid PIBSA described in U.S. Patent No. 5,777,025 and European
20 Patent Application Publication No. EP 542 380; and purified PIBSA described
21 in U.S. Patent No. 5,523,417 and European Patent Application Publication
22 No. EP 602 863. The disclosures of each of these documents is incorporated
23 herein by reference in their entirety.

24 In accordance with the invention, the alkenyl or alkyl succinic anhydride
25 reactant is derived from a polyolefin having a Mn from 1000 to 5000 and a
26 Mw/Mn ratio of 1:1 to 5:1. In a preferred embodiment, the alkenyl or alkyl
27 group of the succinimide has an Mn value from 1800 to 3000. Most preferred
28 are alkenyl or alkyl substituents having an Mn of from 2000 to 2500.

29 Suitable polyolefin polymers for reaction with maleic anhydride include
30 polymers comprising a major amount of C₂ to C₅ monoolefin, e.g., ethylene,
31 propylene, butylene, iso-butylene and pentene. The polymers may be
32 homopolymers, such as polyisobutylene, as well as copolymers of two or
33 more such olefins, such as copolymers of: ethylene and propylene, butylene,
34 and isobutylene, etc. Other copolymers include those in which a minor

1 amount of the copolymer monomers (e.g., 1 to 20 mole %), may be a C₄ to C₈
2 nonconjugated diolefin, e.g., a copolymer of isobutylene and butadiene or a
3 copolymer of ethylene, propylene and 1,4-hexadiene, etc.

4 A particularly preferred class of olefin polymers for reaction with maleic
5 anhydride comprises the polybutenes, which are prepared by polymerization
6 of one or more of 1-butene, 2-butene and isobutene. Especially desirable are
7 polybutenes containing a substantial proportion of units derived from
8 isobutene. The polybutene may contain minor amounts of butadiene, which
9 may or may not be incorporated in the polymer. These polybutenes are
10 readily available commercial materials well known to those skilled in the art.
11 Examples of procedures illustrating the preparation of such material may be
12 found, for example, in U.S. Patents Nos. 3,215,707; 3,231,587; 3,515,669;
13 3,579,450; 3,912,764 and 4,605,808, hereby incorporated by reference for
14 their disclosures of suitable polybutenes.

15 The alkenyl or alkylsuccinic anhydride may also be prepared using the
16 so-called highly reactive or high methyl vinylidene polyalkylene, most
17 commonly PIB, such as described in U.S. Patent Nos. 4,152,499; 5,071,919;
18 5,137,980; 5,286,823; 5,254,649; 5,688,887; published International
19 Applications Numbers; WO 9310063-A1; and published European Patent
20 Applications Numbers 0355895-A; and 0587381A, all of which are hereby
21 incorporated by reference in their entirety. Other polyalkenes may also be
22 used including, for example, polyalkenes prepared using metallocene
23 catalysts.

24 25 **(B)(1)(B) THE PIB/UAR COPOLYMER**

26 The PIB/UAR Copolymer of this synthesis reaction is the PIB/UAR
27 Copolymer of this invention and is previously described herein.

28

1 (B)(1)(C) THE POLYAMINE REACTANT

2 The polyamine reactant should have at least three amine nitrogen
3 atoms per mole, and preferably 4 to 12 amine nitrogens per molecule. Most
4 preferred are polyamines having from about 6 to about 10 nitrogen atoms
5 per molecule. The number of amine nitrogen atoms per molecule of
6 polyamine is calculated as follows:

7

$$\begin{array}{lcl} \text{Average number of nitrogen} & = & \frac{\%N \times M_{pa}}{14 \times 100} \\ \text{atoms in molecule of polyamine} & & \end{array}$$

8

9 wherein % N = percent nitrogen in polyamine or polyamine mixture
10 M_{pa} = number average molecular weight of the polyamine or
11 polyamine mixture

12 Preferred polyalkylene polyamines comprise from about 4 to about
13 20 carbon atoms, there being preferably from 2 to 3 carbon atoms
14 per alkylene unit. The polyamine preferably has a carbon-to-nitrogen ratio of
15 from about 1:1 to 10:1. Examples of suitable polyamines that may be used to
16 form the compounds of this invention include the following: TEPA,
17 pentaethylene hexamine, Dow E-100® heavy polyamine (number = 303,
18 available from Dow Chemical Company, Midland, MI.), and Union Carbide
19 HPA-X heavy polyamine (number average molecular weight = 275, available
20 from Union Carbide Corporation, Danbury, CT.). Such amines encompass
21 isomers, such as branched-chain polyamines, and the previously mentioned
22 substituted polyamines, including hydrocarbyl-substituted polyamines. HPA-X
23 heavy polyamine ("HPA-X") contains an average of approximately 6.5 amine
24 nitrogen atoms per molecule. Such heavy polyamines generally afford
25 excellent results.

26 The polyamine reactant may be a single compound but typically will be
27 a mixture of compounds reflecting commercial polyamines. The commercial
28 polyamine will typically be a mixture in which one or several compounds
29 predominate with the average composition indicated. For example, TEPA
30 prepared by the polymerization of aziridine or the reaction of dichloroethylene
31 and ammonia will have both lower and higher amine members, e.g., TETA,
32 substituted piperazines and pentaethylene hexamine, but the composition will

be largely TEPA and the empirical formula of the total amine composition will closely approximate that of TEPA.

Other examples of suitable polyamines include admixtures of amines of various sizes, provided that the overall mixture contains at least 4 nitrogen atoms per molecule. Included within these suitable polyamines are mixtures of diethylene triamine ("DETA") and heavy polyamine. A preferred polyamine admixture reactant is a mixture containing 20% by weight DETA and 80% by weight HPA-X; as determined by the method described herein, this preferred polyamine reactant contains an average of about 5.2 nitrogen atoms per mole.

Methods of preparing polyamines and their reactions are detailed in Sidgewick's THE ORGANIC CHEMISTRY OF NITROGEN, Clarendon Press, Oxford, 1966; Noller's CHEMISTRY OF ORGANIC COMPOUNDS, Saunders, Philadelphia, 2nd Ed., 1957; and Kirk-Othmer's ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, 2nd Ed., especially Volumes 2, pp. 99-116.

C. POST-TREATMENTS

The polysuccinimide prepared using the PIB/UAR copolymer may be post-treated with a wide variety of post-treating reagents. U.S. Pat. No. 4,234,435, the disclosure of which is incorporated herein by reference, discloses reacting succinic acylating agents with a variety of reagents to give post-treated carboxylic acid derivative compositions that are useful as polysuccinimides and detergents in lubricating oil compositions.

For example, the dispersancy of the polysuccinimide prepared using the PIB/UAR copolymer may be improved by reaction with a cyclic carbonate. This may result in some reduction in fluorocarbon elastomer compatibility. However, this may generally be more than offset by reducing the concentration of the carbonated post-treated polymer in light of the increased dispersancy. The resulting modified polymer has one or more nitrogens of the polyamino moiety substituted with a hydroxy hydrocarbyl oxycarbonyl, a hydroxy poly(oxyalkylene) oxycarbonyl, a hydroxyalkylene, hydroxyalkylenepoly(oxyalkylene), or mixture thereof.

The cyclic carbonate post-treatment may be conducted under conditions sufficient to cause reaction of the cyclic carbonate with secondary

1 amino group of the polyamino substituents. Typically, the reaction is
2 conducted at temperatures of about from about 0 degree C. to about
3 250 degrees C., preferably from about 100 degrees C. to about 200 degrees
4 C. and most preferred from about 50 degrees C. to about 180 degrees C.

5 The reaction may be conducted neat, wherein both the polymer and
6 the cyclic carbonate are combined in the proper ratio, either alone or in the
7 presence of a catalyst (such as an acidic, basic or Lewis acid catalyst).
8 Examples of suitable catalysts include, for example, phosphoric acid, boron
9 trifluoride, alkyl or aryl sulfonic acid, alkali or alkaline carbonate. The same
10 solvents or diluents as described herein with respect to the preparing the
11 PIB/UAR copolymer may also be used in the cyclic carbonate post-treatment.

12 The reaction of polyamino alkenyl or alkyl succinimides with cyclic
13 carbonates is known in the art and is described in U.S. Pat. No. 4,612,132,
14 hereby incorporated by reference, in its entirety. Generally, the procedures
15 described to post-treat polyamino alkenyl or alkyl succinimides with cyclic
16 carbonates may also be applied to post treat the PIB/UAR copolymer.

17 A particularly preferred cyclic carbonate may be 1,3-dioxolan-2-one
18 (ethylene carbonate).

19 The molar charge of cyclic carbonate employed in the post-treatment
20 reaction is preferably based upon the theoretical number of basic nitrogens
21 contained in the polyamino substituent of the succinimide. Thus, when one
22 equivalent of tetraethylene pentamine (TEPA) is reacted with one equivalent
23 of succinic anhydride and one equivalent of the PIB/UAR copolymer, the
24 resulting bis succinimide will theoretically contain 3 basic nitrogens.
25 Accordingly, a molar charge of 2 would require that two moles of cyclic
26 carbonate be added for each basic nitrogen or in this case 6 moles of cyclic
27 carbonate for each mole equivalent of polyalkylene succinimide or
28 succinimide prepared from TEPA. Mole ratios of the cyclic carbonate to the
29 basic amine nitrogen of the polyamino alkenyl succinimide used in the
30 process of this invention are typically in the range of from about 1:1 to about
31 4:1; although preferably from about 2:1 to about 3:1.

32 As described in U.S. Pat. No. 4,612,132, cyclic carbonates may react
33 with the primary and secondary amines of a polyamino alkenyl or alkyl
34 succinimide to form two types of compounds. First, strong bases including

1 unhindered amines such as primary amines and some secondary amines,
2 react with an equivalent of cyclic carbonate to produce a carbamic ester.
3 Second, hindered bases such as hindered secondary amines, may react with
4 an equivalent of the same cyclic carbonate to form a hydroxyalkyleneamine
5 linkage. (Unlike the carbamate products, the hydroxyalkyleneamine products
6 retain their basicity.) Accordingly, the reaction of a cyclic carbonate may yield
7 a mixture of products. When the molar charge of the cyclic carbonate to the
8 basic nitrogen of the succinimide is about 1 or less, a large portion of the
9 primary and secondary amines of the succinimide will be converted to hydroxy
10 hydrocarbyl carbamic esters with some hydroxyhydrocarbylamine derivatives
11 also being formed. As the mole ratio is raised above about 1 increased
12 amounts of poly(oxyalkylene) polymers of the carbamic esters and the
13 hydroxyhydrocarbylamine-derivatives may be produced.

14 The polysuccinimide prepared using the PIB/UAR copolymer and the
15 post-treated polysuccinimide prepared using the PIB/UAR copolymer may
16 also be reacted with boric acid or a similar boron compound to form borated
17 dispersants having utility within the scope of this invention. In addition to boric
18 acid (boron acid), examples of suitable boron compounds include boron
19 oxides, boron halides and esters of boric acid. Generally from about
20 0.1 equivalents to 10 equivalents of boron compound to succinimide may be
21 used.

22 In addition to the carbonate and boric acid post-treatments, the
23 compounds may be post-treated, or further post-treatment, with a variety of
24 post-treatments designed to improve or impart different properties. Such
25 post-treatments include those summarized in columns 27-29 of U.S. Pat.
26 No. 5,241,003, hereby incorporated by reference. Such treatments may
27 include treatment with:

- 28 Inorganic phosphorous acids or anhydrides (e.g., U.S. Pat.
- 29 Nos. 3,403,102 and 4,648,980);
- 30 Organic phosphorous compounds (e.g., U.S. Pat. No. 3,502,677);
- 31 Phosphorous pentasulfides;
- 32 Boron compounds as already noted herein
- 33 (e.g., U.S. Pat. Nos. 3,178,663 and 4,652,387);

- 1 Carboxylic acid, polycarboxylic acids, anhydrides and/or acid halides
- 2 (e.g., U.S. Pat. Nos. 3,708,522 and 4,948,386);
- 3 Epoxides polyepoxiates or thioepoxides
- 4 (e.g., U.S. Pat. Nos. 3,859,318 and 5,026,495);
- 5 Aldehyde or ketone (e.g., U.S. Pat. No. 3,458,530);
- 6 Carbon disulfide (e.g., U.S. Pat. No. 3,256,185);
- 7 Glycidol (e.g., U.S. Pat. No. 4,617,137);
- 8 Urea, thourea or guanidine (e.g., U.S. Pat. Nos. 3,312,619; 3,865,813;
- 9 and British Patent GB 1,065,595);
- 10 Organic sulfonic acid (e.g., U.S. Pat. No. 3,189,544 and
- 11 British Patent GB 2,140,811);
- 12 Alkenyl cyanide (e.g., U.S. Pat. Nos. 3,278,550 and 3,366,569);
- 13 Diketene (e.g., U.S. Pat. No. 3,546,243);
- 14 A diisocyanate (e.g., U.S. Pat. No. 3,573,205);
- 15 Alkane sultone (e.g., U.S. Pat. No. 3,749,695);
- 16 1,3-Dicarbonyl Compound (e.g., U.S. Pat. No. 4,579,675);
- 17 Sulfate of alkoxylated alcohol or phenol (e.g., U.S. Pat. No. 3,954,639);
- 18 Cyclic lactone (e.g., U.S. Pat. Nos. 4,617,138; 4,645,515; 4,668,246;
- 19 4,963,275; and 4,971,711);
- 20 Cyclic carbonate or thiocarbonate linear monocarbonate or
- 21 polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132;
- 22 4,647,390; 4,648,886; 4,670,170);
- 23 Nitrogen-containing carboxylic acid (e.g., U.S. Pat. 4,971,598 and
- 24 British Patent GB 2,140,811);
- 25 Hydroxy-protected chlorodicarbonyloxy compound
- 26 (e.g., U.S. Pat. No. 4,614,522);
- 27 Lactam, thiolactam, thiolactone or dithiolactone
- 28 (e.g., U.S. Pat. Nos. 4,614,603 and 4,666,460);
- 29 Cyclic carbonate or thiocarbonate, linear monocarbonate or
- 30 polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132;
- 31 4,647,390; 4,646,860; and 4,670,170);
- 32 Nitrogen-containing carboxylic acid (e.g., U.S. Pat. No. 4,971,598 and
- 33 British Patent GB 2,440,811);
- 34 Hydroxy-protected chlorodicarbonyloxy compound

- 1 (e.g., U.S. Pat. No. 4,614,522);
- 2 Lactam, thiolactam, thiolactone or dithiolactone
- 3 (e.g., U.S. Pat. Nos. 4,614,603, and 4,666,460);
- 4 Cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate
- 5 (e.g., U.S. Pat. Nos. 4,663,062 and 4,666,459);
- 6 Hydroxyaliphatic carboxylic acid (e.g., U.S. Pat. Nos. 4,482,464;
- 7 4,521,318; 4,713,189);
- 8 Oxidizing agent (e.g., U.S. Pat. No. 4,379,064);
- 9 Combination of phosphorus pentasulfide and a polyalkylene polyamine
- 10 (e.g., U.S. Pat. No. 3,185,647);
- 11 Combination of carboxylic acid or an aldehyde or ketone and sulfur or
- 12 sulfur chloride (e.g., U.S. Pat. Nos. 3,390,086; 3,470,098);
- 13 Combination of a hydrazine and carbon disulfide
- 14 (e.g. U.S. Pat. No. 3,519,564);
- 15 Combination of an aldehyde and a phenol
- 16 (e.g., U.S. Pat. Nos. 3,649,229; 5,030,249; 5,039,307);
- 17 Combination of an aldehyde and an O-diester of dithiophosphoric acid
- 18 (e.g., U.S. Pat. No. 3,865,740);
- 19 Combination of a hydroxyaliphatic carboxylic acid and a boric acid
- 20 (e.g., U.S. Pat. No. 4,554,086);
- 21 Combination of a hydroxyaliphatic carboxylic acid, then formaldehyde
- 22 and a phenol (e.g., U.S. Pat. No. 4,636,322);
- 23 Combination of a hydroxyaliphatic carboxylic acid and then an aliphatic
- 24 dicarboxylic acid (e.g., U.S. Pat. No. 4,663,064);
- 25 Combination of formaldehyde and a phenol and then glycolic acid
- 26 (e.g., U.S. Pat. No. 4,699,724);
- 27 Combination of a hydroxyaliphatic carboxylic acid or oxalic acid and
- 28 then a diisocyanate (e.g. U.S. Pat. No. 4,713,191);
- 29 Combination of inorganic acid or anhydride of phosphorus or a partial
- 30 or total sulfur analog thereof and a boron compound
- 31 (e.g., U.S. Pat. No. 4,857,214);
- 32 Combination of an organic diacid then an unsaturated fatty acid and
- 33 then a nitrosoaromatic amine optionally followed by a boron compound
- 34 and then a glycolating agent (e.g., U.S. Pat. No. 4,973,412);

- 1 Combination of an aldehyde and a triazole
- 2 (e.g., U.S. Pat. No. 4,963,278);
- 3 Combination of an aldehyde and a triazole then a boron compound
- 4 (e.g., U.S. Pat. No. 4,981,492);
- 5 Combination of cyclic lactone and a boron compound
- 6 (e.g., U.S. Pat. No. 4,963,275 and 4,971,711).
- 7

8 **D. LUBRICATING OIL COMPOSITIONS**

9 The PIB/UAR copolymer, polysuccinimides made using the PIB/UAR
10 copolymer and post-treated polysuccinimides made using the PIB/UAR
11 copolymer all of which are described herein are useful as detergent and
12 dispersant additives when used in lubricating oils. When used as detergents
13 or dispersants, these additives may be used at about 0.2 to about 10 wt. % of
14 the total lubricating oil composition and preferably at about 0.5 wt. % to about
15 8 % wt. % and more preferably at about 1 wt. % to about 6 wt. % of the total
16 lubricating oil composition.

17 The lubricating oil used with these additive compositions may be
18 mineral oil or synthetic oils of lubricating viscosity and preferably suitable for
19 use in the crankcase of an internal combustion engine. Crankcase lubricating
20 oils ordinarily have a viscosity of about 1300 cSt at 0 degrees F. to 22.7 cSt at
21 210 degrees F. (99 degrees C.). The lubricating oils may be derived from
22 synthetic or natural sources. Hydrocarbon synthetic oils may include, for
23 example, oils prepared from the polymerization of ethylene,
24 i.e., polyalphaolefin or PAO, or from hydrocarbon synthesis procedures using
25 carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process.
26 Mineral oil for use as the base oil in this invention may include paraffinic,
27 naphthenic and other oils that are ordinarily used in lubricating oil
28 compositions. Synthetic oils include both hydrocarbon synthetic oils and
29 synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of
30 alpha olefins having the proper viscosity. The hydrogenated liquid oligomers
31 of C₆ to C₁₂ alpha olefins such as 1-decene trimer are especially useful. Alkyl
32 benzenes of proper viscosity, such as didodecyl benzene may also be used.

33 Hydrocarbon oils blended with synthetic oils may also be useful. For
34 example, blends of 10 to 25 wt. % hydrogenated 1-decene trimer with

1 75 to 90 wt. % 150 SUS (100 degrees F.) mineral oil are preferred as a
2 lubricating oil base.

3 Lubricating oil concentrates are also envisioned. These concentrates
4 usually include from about 90 wt. % to about 10 wt. %, preferably from about
5 90 wt. % to about 50 wt. %, of an oil of lubricating viscosity and from about
6 10 wt. % to about 90 wt. %, preferably from about 10 wt. % to about 50 wt. %, of the additives described herein. Typically, the concentrates contain sufficient
7 diluent to make them easy to handle during shipping and storage. Suitable
8 diluents for the concentrates include any inert diluent, preferably an oil of
9 lubricating viscosity, so that the concentrate may be readily mixed with
10 lubricating oils to prepare lubricating oil compositions. Suitable lubricating oils
11 that may be used as diluents typically have viscosity in the range from about
12 35 to about 500 Saybolt Universal Seconds (SUS) at 100 degrees F.
13 (38 degrees C.), although any oil of lubricating viscosity may be used.

14 Other additives that may be used include rust inhibitors, foam
15 inhibitors, corrosion inhibitors, metal deactivators, pour point depressants,
16 antioxidants, and a variety of other well-known additives.

17 It is also contemplated that the additives described herein may be
18 employed as dispersants and detergents in hydraulic fluids, marine crankcase
19 lubricants and the like. When so employed, the additive is added at from
20 about 0.1 to 10 % by weight to the oil. Preferably, at from 0.5 to 8 wt. %.

21 22 23 **E. FUEL COMPOSITIONS**

24 The proper concentration of the additive described herein that are
25 necessary to achieve the desired detergency in fuel compositions is
26 dependent upon a variety of factors including the type of fuel used, the
27 presence of other detergents or dispersants or other additives, etc. Generally,
28 however, the range of additive concentration in the base fuel is 10 to
29 10,000 weight parts per million, preferably from 30 to 5000 parts per million of
30 the additive per part of base fuel. If other detergents are present, a lesser
31 amount of the additive may be used. The additives described herein may be
32 formulated as a fuel concentrate, using an inert stable oleophilic organic
33 solvent boiling in the range of about 150 degrees F. to about 400 degrees F.
34 An aliphatic or an aromatic hydrocarbon solvent is preferred. Preferred

1 solvents include benzene, toluene, xylene or higher-boiling aromatics or
2 aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as
3 isopropanol, isobutylcarbinol, n-butanol and the like, in combination with
4 hydrocarbon solvents are also suitable for use with the fuel additive. In the
5 fuel concentrate, the amount of the additive will be ordinarily be about 5 or
6 more wt. % and generally not exceed about 70 wt. %, preferably from about
7 5 wt. % to about 50 wt. % and more preferably from about 10 wt. % to about
8 25 wt. %.

10 **F. SURFACE SIZING AGENTS**

11 It is also contemplated that the PIB/UAR copolymers described herein
12 may be used as is or as an intermediate for surface sizing agents for paper
13 products.

15 **G. POUR POINT DEPRESSANTS**

16 It is also contemplated that the PIB/UAR copolymers described herein
17 may be used as is or as an intermediate for pour point depressants.

18 * * *

21 The following examples are included to demonstrate preferred
22 embodiments of the invention. It should be appreciated by those of skill in the
23 art that the techniques disclosed in the examples that follow may represent
24 techniques discovered by the inventor to function well in the practice of the
25 invention, and thus may be considered to constitute preferred modes for its
26 practice. However, those of skill in the art should, in light of the present
27 disclosure, appreciate that many changes may be made in the specific
28 embodiments that are disclosed and still obtain a like or similar result without
29 departing from the spirit and scope of the invention.

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1 had a SAP number of 210mg KOH/g sample. The M_n of this product was
2 1642, and the M_w was 2250 as determined by GPC.

3

4

Example 3

5

C₁₄ Alpha Olefin/Ma Copolymer Prepared In An Aromatic Solvent

6

7

8

A mixture was prepared by adding 60.45g C₉ aromatic solvent to
9 49.31g tetradecene-1 (0.251 mol). After adding 22.17g maleic anhydride
10 (0.226 mol) to this mixture, the resulting mixture was heated to 130 degrees
11 C. overnight to remove any water. Then a mixture of 22.17g maleic anhydride
12 (0.226 mol) and 0.54g di-tert-butyl peroxide (3.7 mmol) was added in
13 three equal portions over 1 hour to the dehydrated
14 solvent/tetradecene-1/maleic anhydride mixture. The resulting mixture was
15 heated overnight at 135 degrees C. Then the solvent was removed in a
16 vacuum. A total of 67.09g product was obtained. The SAP number for this
17 product was 288mg KOH/g sample. The M_n for this sample was 4188 and the
18 M_w was 7334.

19

20

Example 4

21

C₁₄ Alpha Olefin/MA Copolymer Prepared Without Solvent

22

23

24

A mixture was prepared by adding 74.51g maleic anhydride
25 (0.760 mol) to 300.91 g tetradecene-1 (1.532 mol). This mixture was heated
26 to 131 degrees C., and 1.1g di-tert-butyl peroxide (75 mmol) was added in
27 5 equal portions over three hours. Then the temperature was raised to
28 150 degrees C., and the reaction was continued overnight. The product of
29 this reaction was then stripped in a vacuum to remove any unreacted
30 tetradecene-1. This product had a SAP number of 199mg KOH/g sample,
31 had a M_n of 14010, and a M_w of 33900.

32

33

34

35

Examples 5-8 show that low molecular weight PIB/UAR copolymer may
be prepared using the C₁₂-C₂₈ PIB without any aromatic solvent. A heel
process, as described herein was used.

1 **Example 5**

2 **C₁₂-C₂₈ PIB/UAR Copolymer Prepared**
3 **Using A Heel Process and No Additional Solvent**
4

5 A mixture was prepared by adding 30.02g of C₁₂-C₂₈ PIB (0.143 mol) to
6 30.02g of C₁₂-C₂₈ PIB/UAR copolymer that was prepared as described in
7 Example 2. While stirring this mixture, 12.61g maleic anhydride (0.129 mol)
8 was added. Then, five equal portions of 0.212g of di-tert-butyl peroxide
9 (1.45 mmol) were added to the PIB/PIB/UAR copolymer/maleic anhydride
10 mixture over 2.5 hours. The temperature was then increased to 150 degrees
11 C. and held there overnight. This process resulted in a product that had M_n of
12 1487, a M_w of 2452, and had a SAP number of 254mg KOH/g sample.
13

14 **Example 6**

15 **Additional C₁₂-C₂₄ PIB/UAR**
16 **Copolymer Prepared Using The Heel Process**
17

18 A mixture was prepared by adding 38.33g of C₁₂-C₂₈ PIB (0.183 mol) to
19 38.37g of PIB/UAR copolymer prepared as directed in Example 5. This
20 mixture was heated to 100 degrees C. While stirring the mixture, 16.10g
21 maleic anhydride (0.164 mol) was added. Over three hours, 0.265g
22 di-tert-butyl peroxide was added in five equal portions. The temperature was
23 then increased to 150 degree C and held there overnight. The product from
24 this reaction had a SAP number of 250mg KOH/g sample, a M_n of 1471, and a
25 M_w of 2502.
26

27 **Example 7**

28 **Additional C₁₂-C₂₄ PIB/UAR**
29 **Copolymer Prepared Using The Heel Process**
30

31 Example 6 was repeated using 63.44 g of the PIB/UAR copolymer from
32 Example 6, 63.63g C₁₂-C₂₈ PIB (0.309 mol), and 27.26 g maleic anhydride
33 (0.278 mol). Di-tert-butyl peroxide 0.45g (3 mmol) was added as in described
34 in Example 6. The product from this reaction had a SAP number of 262.5, a
35 M_n of 1578, and a M_w of 2691.
36

Table 2

Table 2 includes chemical and physical properties for low molecular weight PIB/UAR copolymers prepared with and without solvent, low molecular weight PIB/UAR copolymers prepared using the heel process, and alpha olefin copolymers prepared with and without solvent. The results of Examples 1, 2, 3, 4, 5, 6 and 7 are presented in Table 2 and show that even with a solvent, using C₁₄ alpha olefin to prepare a copolymer produced a copolymer that was higher in molecular weight than the PIB/UAR copolymer that was prepared using the C₁₂-C₂₈ PIB with or without solvent when the heel process is used. Note that PIB/UAR copolymers are liquid at ambient temperature, whereas alpha olefin copolymers are solid at ambient temperature.

Example	Starting material	Physical Properties of Copolymer	Presence of Solvent or Heel Process	M _n by GPC	M _w by GPC	SAP No. Mg KOH/g sample
1	Low Molecular Weight PIB	Liquid	solvent	930	1851	290
2	Low Molecular Weight PIB	Liquid	solvent	1642	2250	210
3	Alpha olefin	Solid	solvent	4188	7334	288
4	Alpha olefin	Solid	Without solvent	14010	33900	199
5	Low Molecular Weight PIB	Liquid	Heel Process Without Solvent	1487	2452	254
6	Low Molecular Weight PIB	Liquid	Heel Process Without Solvent	1471	2502	250
7	Low Molecular Weight PIB	Liquid	Heel Process Without Solvent	1578	2691	262.5

Example 8

A Polysuccinimide Prepared Using The C₁₂-C₂₈ PIB/UAR Copolymer

A mixture was prepared by adding 229.06g PIBSA 2300 (SAP number 50.4 mg KOH/g sample, 0.103 mole), 226.79g diluent oil, and 17.10g of the C₁₂-C₂₈ PIB/UAR copolymer from Example 1 (SAP number 290 mg KOH/g sample, 0.0442 mole) to a three neck flask equipped with a mechanical stirrer, nitrogen inlet, Dean Stark trap, and heating mantle. The PIBSA to PIB/UAR copolymer ratio was 70/30 on an anhydride basis. This means that there were 70 moles of PIBSA anhydride to 30 moles of PIB/UAR anhydride. After this mixture was heated to 100 degrees C., 21.21g HPA (0.0771 mole) was added while stirring for 1 hour. The amine/anhydride CMR was 0.525. This mixture was heated to 165°C for 72 hours. A polysuccinimide was formed that had 1.45 %N, 31.0 TBN, 0.24 TAN, haze of 2.8%, and a viscosity at 100 degrees C of 153 cSt.

Example 9 and 10

Other Polysuccinimides Were Prepared

The procedure for Example 8 was repeated except that different amines and different amine/anhydride CMR was used. The chemical and physical properties for these products are shown in Table 3.

Table 3

Table 3 includes chemical and physical properties for polysuccinimides made with a 70 to 30 ratio of PIBSA to PIB/UAR copolymer on an anhydride basis and C₁₂-C₂₈ PIB/UAR copolymer. The results from Examples 8-10 show that a polysuccinimide may be prepared using the C₁₂-C₂₈ PIB/UAR copolymer prepared as directed in these examples.

Example	Amine	Amine/PIBS A CMR	%N	TBN	Vis @ 100°C	TAN	haze
8	HPA	0.525	1.45	31.0	153	0.24	2.8
9	TETA	0.5	0.82	11.3	160	0.97	0.8
10	HPA	0.5	1.35	28.1	165	0.67	1.2

Example 11
Polysuccinimide Post
Treatment Using Ethylene Carbonate

A mixture was prepared by adding 23.62g (0.27 mole) of ethylene carbonate to 185.65g of a polysuccinimide prepared as described in Example 8. This mixture was prepared in a three-neck flask equipped with a mechanical stirrer, a heating mantle and a nitrogen inlet at 165 degrees C. while the mixture was being stirred. The EC/BN CMR was 2.0. This mixture was heated for 14 hours. The product had 1.37 %N, 17.6 TBN, 0.20 TAN, haze of 11.0%, and a viscosity at degrees C. of 426 cSt.

Example 12-13
Preparation Of Other
Post-treated Polysuccinimides

Polysuccinimides of Examples 8, 9, and 10 were post treated as directed in Example 11.

Table 4

The chemical and physical properties of the post-treated polysuccinimides of Examples 11- 13 are shown in Table 4.

Post-treated Polysuccinimides	Polysuccinimide from Example	%N	TBN	Viscosity @ 100°C	TAN	Haze
11	8	1.37	17.6	426	0.2	11.0
12	9	0.81	7.5	182	<0.05	5.7
13	10	1.29	16.3	372	0.06	6.1

Example 14
Polysuccinimide Prepared
Using C₁₂-C₂₈ PIB/UAR Copolymer

A mixture was prepared by adding 49.9g PIB/UAR copolymer prepared according to example 1 (SAP 290mg KOH/g sample 0.129 mole) to 1125g of a mixture of sulfonic acid catalyzed PIBSA 2300 and diluent oil

1 (SAP number 30 mg KOH/g sample, 0.30 mole) and 375g of additional diluent
2 oil in a three neck flask equipped with an overhead stirrer, heating mantle,
3 and Dean Stark trap. The PIBSA to PIB/UAR copolymer ratio was 70/30 on
4 an anhydride basis. This mixture was heated to 100 degrees C., and
5 59.08g HPA (0.215 mole) was added. The amine/anhydride CMR was
6 0.5. This mixture was heated for 6 hours at 170 degrees C. and then cooled to
7 100 degrees C. A total of 7.2ml water was collected over the 6-hour period.
8 The product from this reaction was then reacted with 180.87g of ethylene
9 carbonate (2.06 mole) that was added over 1.5 hours. This product/ethylene
10 carbonate mixture was heated to 170°C for 14 hours. The product from this
11 reaction had 1.22 %N, TBN 15.7, TAN 1.05, viscosity at 100 degrees C.
12 254 cSt, and a haze of 11.9%.

13 14 **Example 15**

15 **Polysuccinimide Prepared Using C₁₂-C₂₈** 16 **PIB/UAR Copolymer Using A Two Step Process** 17

18 A mixture was prepared by adding 5.96g HPA (21.7 mmole) to a
19 solution of 102.86g sulfonic acid catalyzed PIBSA 2300 (SAP 52.5 mg KOH/g
20 sample, 48 mmole) and diluent oil 97.14g in a three neck flask equipped with
21 an overhead stirrer, heating mantle and Dean Stark trap. After heating this
22 mixture at 160°C for four hours, 8.6g of the C₁₂-C₂₈ PIB/UAR copolymer from
23 example 2 (SAP 210 mg KOH/g sample, 16 mmole) was added drop wise
24 over 30 minutes. The PIBSA to PIB/UAR copolymer ratio was 75/25 on an
25 anhydride basis. Then an additional 1.98g (7.2 mmole) of HPA was added to
26 the mixture. The mixture was then heated at 160 degrees C. overnight. The
27 amine/anhydride CMR was 0.45. The product from this reaction had
28 1.30 %N, and had a viscosity at 100 degrees C. of 234 cSt.

29 30 **Example 16**

31 **Soot Thickening Bench Test Results For Polysuccinimides And** 32 **Post-treated Polysuccinimides Made From C₁₂-C₂₈ PIB/UAR Copolymer** 33

34 The polysuccinimides and post-treated polysuccinimides from
35 Examples 8-13 were reacted in the soot thickening bench test. In this test

98.0 g of the test sample was weighed and placed into a 250-milliliter beaker. To this was added 2.0 g Vulcan XC-72R.TM. carbon black from Cabot Co. The mixture was stirred and then stored for 16 hr in a desiccator. A second sample without the carbon black, was mixed for 60 sec. using a Willems Polytron Homogenizer--Model PF 45/6 and then degased in a vacuum oven for 30 minutes at 50 to 55 degrees C. The viscosity of the two samples was then measured at 100 degrees C. using a capillary viscometer. The percent viscosity increase was calculated by comparing the viscosity of the samples with and without carbon black. Thus the lower the percent viscosity increase the better the dispersancy of the dispersant. The results from the soot thickening bench test are shown in Table 5.

Table 5

Table 5 includes soot thickening bench test results for polysuccinimide made from C₁₂-C₂₈ PIB/UAR copolymer. Based on the soot thickening bench tests, Examples 8-13 show that the best soot thickening results were obtained when the amine was HPA instead of TETA, and when EC post treatment was used.

Example	Amine/anhydride CMR	Amine	EC/BN CMR	% Viscosity Increase
8	0.525	HPA	0	100
9	0.525	HPA	2	29
10	0.5	TETA	0	267
11	0.5	TETA	2	135
12	0.5	HPA	0	111
13	0.5	HPA	2	36

Example 17

Samples were tested in the ASTM D-5967-99A extended version (Mack T-8E) diesel engine oil test. This test evaluates the soot handling capability of a engine crankcase oil with regard to viscosity. In other words, this test evaluates a oil's ability to control viscosity increase due to

1 soot loading in the oil. In general, a lower viscosity increase indicates
2 superior performance.

3 The field service simulated was heavy-duty, stop and go operation with
4 high-soot loading. The test engine was a Mack E7-350, fixed time, in-line
5 six cylinder configuration 11GBA77623, open-chamber, four-stroke,
6 turbocharged, intercooled, compression ignition engine. The bore and
7 stroke are 4 7/8 x 6 1/2 inches. The engine was rated at
8 350 bhp @ 1800 rpm. Each test was 300 hours under constant rated
9 speed and load conditions with controlled water out, fuel, intake air and
10 intake manifold temperatures. Exhaust back pressure and inlet air
11 restriction levels was also controlled. Between tests, the engine was
12 flushed for 2 hours with the next test oil. The oil filter was also checked for
13 plugging. Oil samples were taken every 25 hours and analyzed for
14 kinematic viscosity at 100 degrees C. The passing limit for EO-M+ was
15 1.8 relative vis @ 4.8% soot; 0.5 slope at 4.8% soot; and 0.75 slope at
16 275 hrs or 5.8% soot. The passing limit for CH-4 was 2.1 relative
17 vis @ 4.8% soot; 0.75 slope at 4.8% soot; and 1.0 slope at 275 hrs or
18 5.8% soot.
19

Table 6

Table 6 includes Mack T-8E diesel engine oil test results for fully formulated oils comprising either sample A or B, detergent, zinc dithiophosphate wear inhibitor, oxidation inhibitor, other inhibitors and other commonly used additives in a group 1 base oil with VI improver to give 15W40 type oil. Sample A is a polysuccinimide prepared from an alpha olefin copolymer in solid form and Sample B is a polysuccinimide prepared from a low molecular weight PIB/UAR copolymer of this invention. Based on the Mack T-8E diesel engine oil tests, Sample B had equivalent performance to Sample A.

SAMPLE	A	B	EO-M⁺ limit	CH-4 limit
250 hr Soot %	5.4	5.8		
300 hr Soot %	6.2	6.9		
Relative vis @ 4.8% soot	1.42	1.53		
Severity adjustment	0.24	0.19		
Adjusted relative vis at 4.8% soot	1.66	1.72	1.8	2.1
Slope @ 4.8% soot	0.15	0.38	0.5	0.75
Slope @ 275 hrs or 5.8% soot	0.31	0.70	0.75	1.0